[Contribution from the Chemical Laboratory of Harvard University]

The Slow Hydrolysis of Ferric Chloride in Dilute Solution. II. The Change in Hydrogen Ion Concentration

By Arthur B. Lamb and Alfred G. Jacques

In a previous article[1] we presented data as to the changing conductance, color and chloride ion concentration of dilute solutions of ferric chloride and were able to draw from these data certain conclusions with regard to the slow hydrolysis which takes place in them. Direct and unequivocal information as to the hydrogen ion concentration in these solutions is, however, essential to a more complete understanding of this phenomenon and this we have now secured by measurements of the electromotive force exerted by glass electrodes in these solutions during the course of the slow hydrolysis. Glass electrodes adjust themselves rapidly under these conditions and, in contrast with the ordinary hydrogen electrode which Browne[2] used in similar solutions, with only partial success, are quite unaffected by the ferrous–ferric oxidation potential.

Apparatus and Procedure.—The form of glass electrode employed was that of MacInnes and Dole[3] and the components of the cell whose potential (E_x) we have measured for this purpose, were arranged as follows

$$\text{Ag/AgCl, 0.1 } M \text{ HCl/glass/FeCl}_3 \text{ soln./KCl satd. soln./HgCl} + \text{KCl satd. soln./Hg}$$

The ferric chloride solution was replaced at frequent intervals by a standard phthalate-hydrochloric acid buffer and the potential (E_B) again measured. Knowing the hydrogen ion activity of the buffer (H_B), that of the ferric chloride solution (H_x) was calculated by the usual Nernst equation

$$E_x - E_B = 0.0592 \log (H_x/H_B)$$

The apparatus used was very similar to that described by MacInnes and Belcher[4a] and included a Cambridge Instrument Co. Compton electrometer and a type K Leeds and Northrup potentiometer. The cell used in most of the experiments is shown in Fig. 1. It was placed in a water thermostat maintained at 25 ± 0.05°. The silver–silver chloride electrodes were prepared according to the procedure of MacInnes and Parker[4b] except that a single platinum wire instead of a platinum gauze was employed. The electrodes, immersed in the same electrolyte, were found to give the same potential to within less than a millivolt.

In making a series of measurements the sensitivity and symmetry of the electrometer were first ascertained and if necessary re-adjusted. The potential of the cell, filled with the buffer, was also measured. The ferric chloride solution was then prepared from dry, anhydrous ferric chloride in the manner described in our previous communication.[1] A portion was poured into the U-tube B already in place in the thermostat; the salt-bridge A and the glass electrode E with the silver–silver chloride electrode E already inserted and connected to the potentiometer were then placed in position and a reading was taken immediately. Owing to the inertia of the electrometer it usually was not possible to obtain this reading sooner than two minutes after the start of the solution process. At the beginning, when the potential was changing rapidly, it was inconvenient to balance the potentiometer; instead the potential was calculated from the slightly unbalanced potentiometer reading and the deflections of the electrometer. After a few minutes when the potential had ceased to change rapidly, the electrometer was used in the usual way as a null instrument. At intervals, if the measurements were long continued, the tube B was replaced by an exactly similar one containing the standard buffer and its potential again taken.

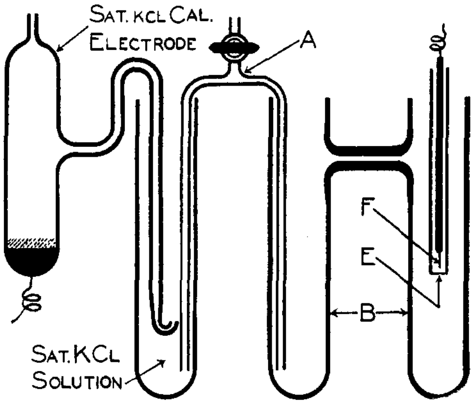

Fig. 1.—Glass electrode cell: A, salt-bridge; B, U-tube; E, glass electrode; F, silver electrode.

The standard buffer had a nominal *p*H of 3.0. Its hydrogen ion activity was determined accurately by comparison with a carefully prepared 0.001000 M solution of hydrochloric acid using the following cell

$$\text{Ag/AgCl, 0.1 } M \text{ HCl/glass/0.001 } M \text{ HCl/KCl satd. soln./buffer/glass/AgCl, 0.1 } M \text{ HCl/Ag}$$

The silver–silver chloride electrodes used in the standardizing measurements placed in the same solution agreed with each other to within 0.0001 v., the sensitivity of the electrometer. The glass electrode also had the same asymmetry potential to within the same limit.

The potential of the cell was −0.0025 v., which, taking the activity coefficient of the hydrochloric acid solution as

---

[1] Lamb and Jacques, This Journal, **60**, 997 (1938). One of us, A. G. Jacques gratefully acknowledges his indebtedness to the Hudson Bay Company for the grant of a fellowship and to Professor M. A. Parker of the University of Manitoba where part of this work was done.

[2] Browne, *ibid.*, **45**, 297 (1923).

[3] Duncan A. MacInnes and Malcolm Dole, *Ind. Eng. Chem., Anal. Ed.*, **1**, 57 (1929).

[4] (a) Duncan A. MacInnes and Donald Belcher, *ibid.*, **5**, 199 (1930); (b) MacInnes and Parker, This Journal, **37**, 1445 (1915).

0.984,[5] gives the hydrogen ion activity of the buffer as pH 3.045.

TABLE I

HYDROGEN ION ACTIVITIES OF 0.00100 N FERRIC CHLORIDE SOLUTION

E_b = 0.0705

Time, min.	E_x, mv.	H^+, m.M
1.5	94.2	0.359
2	92.9	.378
3	91.6	.397
4	90.4	.416
5	89.5	.431
7.5	88.5	.448
9	86.7	.466
10	84.3	.527
15	82.0	.577
20	80.3	.615
25	79.3	.650
30	78.0	.700
40	77.0	.700
60	75.9	.731
90	74.8	.762
120	73.8	.793
180	72.9	.820
300	72.1	.847
480	71.8	.857
1440	71.0	.885

TABLE II

HYDROGEN ION ACTIVITIES OF FERRIC CHLORIDE SOLUTIONS

Concn. $FeCl_3$ $10^3 \times N$	10.0		4.0		2.0		1.0		0.667		0.50	
E_b mv.	65.9		71.3		70.5		70.5		70.0		70.0	
Time, min.	E_x, mv.	H^+, m.M	E_x, mv.	H^+, m.M	E_x, mv.	H^+, m.M	E_x, mv.	H^+, m.M	E_x, mv.	H^+, m.M	E_x, mv.	H^+, m.M
2	56.3	1.31	72.0	0.877	83.8	0.537	92.9	0.378	100.7	0.273	106.5	0.218
3	56.0	1.33	71.5	.896	83.4	.545	91.6	.397	97.7	.308	104.6	.234
4	56.0	1.33	71.5	.896	83.0	.554	90.4	.416	96.1	.326	102.0	.259
5	55.3	1.36	70.7	.923	80.2	.618	89.5	.431	94.4	.349	100.1	.280
7.5	55.2	1.37	69.7	.959	78.1	.671	88.5	.448	91.9	.385	...	...
10	55.2	1.37	68.9	.991	75.5	.743	84.3	.527	90.5	.407	95.0	.341
15	55.1	1.37	67.3	1.06	73.5	.801	82.0	.577	88.4	.441	...	...
20	54.0	1.43	..	...	72.2	.843	80.3	.615	87.0	.466	92.6	.374
25	54.4	1.41	64.6	1.17	70.0	.912	79.3	.640	86.3	.479	...	...
30	54.4	1.41	63.3	1.23	69.3	.944	78.0	.673	85.7	.490	91.0	.398
45	53.6	1.46	60.3	1.38	..	1.06	..	...	84.5	.513	89.9	.416
60	52.2	1.53	58.5	1.48	64.0	1.16	75.9	.731	83.6	.531	89.8	.418
90	50.4	1.64	..	...	61.6	1.27	74.8	.762	81.5	.577	...	...
120	48.1	1.80	54.9	1.71	60.5	1.33	73.8	.793	81.0	.588	...	...
180	43.8	2.13	51.7	1.93	58.3	1.45	72.9	.820	80.5	.600	88.8	.434
240	40.0	2.47	49.1	2.14	57.2	1.51	..	...	80.3	.604	88.5	.438
1440	..	..	43.0	2.71	54.6	1.68	71.0	.885	79.9	.614	88.0	.448
2880	23.0	4.79	42.4	2.77	..	...	..	...	...	...	...	...

The calculated activities in the ferric chloride solutions neglect any residual liquid junction potentials not eliminated by the saturated solution of potassium chloride. This can hardly involve any serious error since, by the method of standardization adopted, all these potentials are eliminated except those between the ferric chloride and the saturated potassium chloride solutions on the one hand, and the standard hydrochloric acid and saturated potassium chloride solutions on the other. Moreover, since the ferric chloride solutions were all very dilute and contained hydrochloric acid of the same order of concentration as the standard (0.001 N), these two residual potentials must have very nearly cancelled.

The accuracy of our measurements under the most favorable conditions was determined by a series of eight measurements made on a ferric chloride solution that had reached equilibrium, the salt-bridge being refilled before each measurement. The average electromotive force was 0.0149 v. with a maximum deviation of ±0.0002 and an average deviation of ±0.0001 v. Since, however, each determination of activity involved two independent measurements, the probable error would be somewhat greater. In the more rapidly changing solutions also an additional error, in the extreme cases perhaps several times as great, would result from changes during the unavoidable time interval required for a measurement.

Results

Measurements were made, usually in duplicate, over a range of concentrations of ferric chloride from 0.01 to 0.0005 N, without and in two instances with the previous addition of acid. Representative numerical data[6] are given in full for a single solution in Table I. The computed hydrogen ion activities for all the solutions measured are summarized in Tables II and III and are shown graphically in Figs. 2 and 3.

Extent of the Final Conversion.—Only in the case of the three most dilute solutions was the final equilibrium closely enough approached during our measurements with the glass electrode to permit an accurate estimation of the hydrogen ion activity at equilibrium. In these cases, after converting the extrapolated activity to concentration by dividing by the activity coefficient of

---

(5) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 336.

(6) The complete numerical data for these and other measurements are available in the Thesis of Dr. Alfred G. Jacques, "The Hydrolysis of Ferric Salt Solutions," Harvard University, Cambridge, Mass., 1931.

Table III

Hydrogen Ion Activities of 0.00100 N Ferric Chloride Solution in Hydrochloric Acid Solution

Concentration HCl......	0.196m.N		0.397m.N	
Time, min.	E_x, mv.	H^+, m.M	E_x, mv.	H^+, m.M
2	97.3	0.469	74.4	0.649
3	96.6	.483	74.2	.653
4	96.3	.489	74.2	.653
5	95.9	.496	74.2	.653
7,5	95.7	.499	74.0[a]	.657
10	94.7	.519	74.4	.649
15	93.2	.550	73.8	.664
20	92.0	.577	73.2	.679
25	90.6	.608		
30	88.7	.655	73.0	.684
40	87.7	.681		
50	86.7	.708		
60	84.3	.778	72.6	.695
75	83.0	.819	72.4	.700
120	79.6	.933	71.0	.740
180	78.6	.971	69.5	.784
240	77.3	1.02	67.3	.853
Last meas.	76.0	1.07	71.0	1.18

[a] Eight minutes.

hydrochloric acid in solutions of the same ionic strength and then in turn dividing by the equivalent concentration of the ferric salt solution, the percentage conversions of 91.4, 94.5 and 93.0%, respectively, in 0.500, 0.667 and 1.000 milliequivalent solutions were found. These are to be compared with the values 95.2, 94.0 and 94.1%, respectively, computed from our conductance measurements and given in Table III and Fig. 10 of our previous communication.[1] The agreement is good except for the most dilute solution where the value computed from our glass electrode measurements appears to be unduly large.

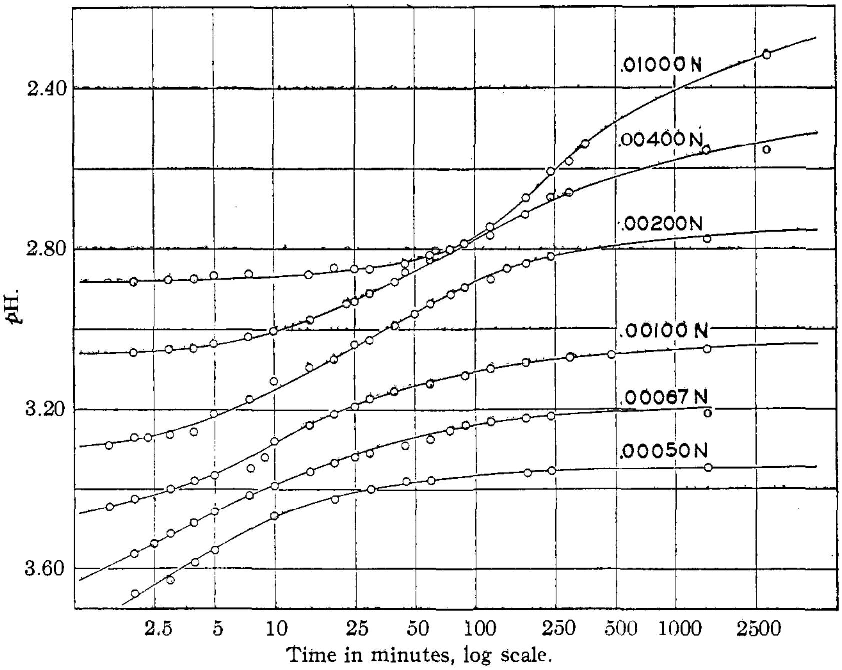

Fig. 2.—Change of pH of ferric chloride solutions with time at 25°.

Interpretation of the Results

The prevailing explanation[7] of the slow hydrolysis of ferric salts is substantially that proposed by Goodwin[8] on the basis of his conductance measurements with ferric chloride solutions. According to it, as soon as the dilute solution is prepared a rapid reversible hydrolysis ensues, giving rise chiefly to $Fe(OH)^{++}$ and H^+. This equilibrium is displaced to give a further hydrolysis by the slow "polymerization" of the basic ferric ions or the ferric hydroxide molecules to form colloidal basic ferric chlorides or hydroxide. Goodwin explained the greater rapidity of this secondary hydrolysis, in dilute solutions than in concentrated solutions, as due to "the much larger proportion of $Fe(OH)^{++}$ or $Fe(OH)_3$" in the dilute solution.

It is, however, clear that a larger proportion or percentage concentration of these substances would not necessarily explain the much greater *absolute* velocity of hydrolysis actually observed in the dilute solutions; such an explanation would require that there be a greater *actual* concentration of the reacting or polymerizing substance in the dilute than in the concentrated solutions.

To ascertain whether this requirement is met by any one of the several immediate hydrolysis products of the ferric chloride and, if so, whether its concentration in the dilute is sufficiently greater than that in the concentrated solutions to account for the increased velocity observed, we have calculated the concentration of these hydrolysis products in a series of solutions rang-

---

(7) (a) Gmelins "Handbuch der anorganischen Chemie," 8th Edition, Iron, Part 13, Verlag Chemie, Berlin, 1929, pp. 272–278. (b) Abegg "Handbuch der anorg. Chemie. IV. Iron and Its Compounds," B187–192 and B788, S. Hirzel, Leipzig, 1930 and 1935.

(8) H. M. Goodwin, *Z. physik. Chem.*, **21**, 1 (1896); also *Technology Quarterly*, **9**, 254 (1896).

ing from 1 × 10^{-2} to 1 × 10^{-6} N. For this calculation a knowledge of the constants of the reversible hydrolysis of the ferric ion is required.

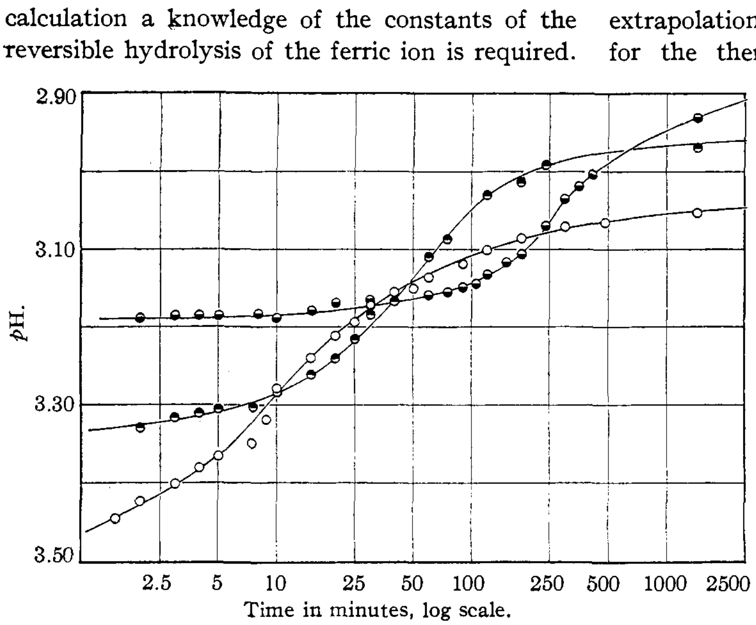

Fig. 3.—Change of pH with time in 0.001 N ferric chloride in the presence of acid: ◒, 0.000397 N HCl; ◓, 0.000196 N HCl; ○, no acid.

The Constants of the Reversible Hydrolysis.—Some information on this score is already available; Bjerrum,[9] recalculating and extrapolating the conductimetric data of Goodwin,[8] obtained concordant values for the hydrolysis constant of ferric chloride in 0.02 to 0.0003 M solutions, assuming only first stage hydrolysis to occur; *i. e.*,

$$k_1 = (H^+)(Fe(OH)^{++})/(Fe^{+++}) = 2.48 \times 10^{-3}$$

This concordance was, however, presumably somewhat illusory, since, assuming the not unusual ratio of 100:1 for the first and second hydrolysis constants, over 7% of the hydrogen ions in the 0.0003 M solution would have resulted from second stage hydrolysis, *i. e.*, from the formation of $Fe(OH)_2^+$.

More recently Bray and Hershey,[10] by comparing data on two equilibria involving ferric nitrate and ferric perchlorate solutions, the one of high, the other of low concentrations, have computed k_1 to be 4.86 × 10^{-3} in 0.00033 M solution or 6.0 ± 0.5 × 10^{-3} at zero ionic strength (also neglecting any second stage hydrolysis).

To obtain independent and more direct evidence as to the extent of this reversible hydrolysis, we have utilized our measurements made with the glass electrode in the ferric salt solutions during the initial stages of the slow hydrolysis. After extrapolation to zero time the resulting values for the thermodynamic hydrogen ion concentrations have been converted to actual concentrations by estimating the ionic strength of the partially hydrolyzed solution and dividing by the corresponding activity coefficient of the hydrogen ion as tabulated by Lewis and Randall[11] based on the assumption of equal activity coefficients of the potassium and chloride ions.

Assuming complete ionization of the strong electrolytes and neglecting any third stage hydrolysis, as is justifiable both on theoretical grounds and on the basis of our colorimetric measurements, the expression

$$k_1 = \frac{(H^+)^2((H^+) - S)}{m((H^+) + 2k_2) - ((H^+) + k_2)((H^+) - S)}$$

can be derived, where (H^+) represents the concentration of the hydrogen ion, m that of the salt and S that of the added acid. By trial and error an approximate value of k_2 was found, namely, $k_2 = 2 \times 10^{-5}$, such as would give values of log k_1, which when plotted against the square root of the ionic strength lay reasonably upon a straight line of the usual slope. Variations in the value of k_2 exert only a very slight effect upon the value of k_1 in the more concentrated, but a considerable effect in the more dilute, solutions.

The resulting values of k_1 are given in Table IV and are plotted in Fig. 4.

Table IV

k_1 from Glass Electrode Measurements

Without Added Acid

$m \times 10^3$	(H^+) obsd. $\times 10^3$	$\mu^{1/2}$	(H^+) corr. $\times 10^3$	$k_1 \times 10^3$
3.333	1.35	0.128	1.48	1.15
1.333	0.835	.0787	0.887	1.79
0.667	.472	.0548	.489	1.23
.3333	.302	.0387	.310	2.76
.2222	.208	.0300	.212	2.02
.1667	.163	.0257	.1655	2.32

With Added Acid

$m \times 10^3$	$S \times 10^3$	(H^+) obsd. $\times 10^3$	$\mu^{1/2}$	(H^+) corr. $\times 10^3$	$k_1 \times 10^3$
0.3333	0.197	0.462	0.0406	0.481	2.38
.3333	.400	.647	.0435	.669	2.56

The results with added acid are presumably

---

(9) N. Bjerrum, *Z. physik. Chem.*, **59**, 350 (1907).

(10) Bray and Hershey, This Journal, **56**, 1889 (1934).

(11) Lewis and Randall, "Thermodynamics," p. 382.

the more accurate, as they are least subject to error in extrapolation to zero time.

We have also computed k_1 from our measurements of conductance with and without the prior addition of acid, but the results are less certain because the conductivities of unhydrolyzed $FeCl_3$, and of $FeOHCl_2$ and $Fe(OH)_2Cl$, are not accurately known. We have assumed them to be the same as the known conductivities of the corresponding salts $LaCl_3$, $SrCl_2$ and NaCl[12] at the same equivalent concentrations. We have taken k_2 as 2×10^{-5} from our measurements with the glass electrode.

For the sake of simplicity the almost negligible concentration of $Fe(OH)_2^+$ was computed from the known concentration of hydrogen ion in these solutions using the relation

$$(\mathrm{Fe(OH)_2}^+) = \frac{((\mathrm{H}^+) - S)}{2 + (\mathrm{H}^+)/k_2}$$

where S represents the concentration of hydrogen ion added, if any, and where the almost infinitesimal concentration of $Fe(OH)_3$ formed in the initial, instantaneous hydrolysis is neglected. The concentration of the $Fe(OH)^{++}$ can then be expressed in known terms as follows

$$(\mathrm{Fe(OH)}^{++}) = \frac{1000h - (S\mu_{\mathrm{HCl}} + m\mu_{\mathrm{FeCl_3}}) - (\mathrm{Fe(OH)_2}^+)(\mu_{\mathrm{Fe(OH)_2Cl}} + 2\mu_{\mathrm{HCl}} - \mu_{\mathrm{FeCl_3}})}{\mu_{\mathrm{Fe(OH)Cl_2}} + \mu_{\mathrm{HCl}} - \mu_{\mathrm{FeCl_3}}}$$

where h represents the specific conductance of the solution extrapolated to zero time and S the concentration of the added acid.

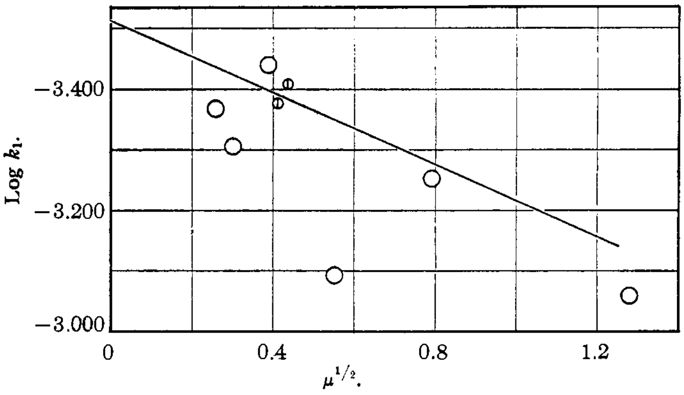

Fig. 4.—First hydrolysis constant (k_1).

Table V

k_1 from Conductance Measurements at 25°

FeCl₃			Fe(NO₃)₃			FeCl₃ with prior addition of HCl			
Concn. $\times 10^3$ M	Spec. cond. 1/ohm $\times 10^3$	k_1 $\times 10^3$	Concn. $\times 10^3$ M	Spec. cond. 1/ohm $\times 10^3$	k_1 $\times 10^3$	Concn. $FeCl_3$ $\times 10^3$ M	Concn. HCl $\times 10^3$ M	Spec. cond. 1/ohm $\times 10^3$	k_1 $\times 10^3$
3.333	1.745	2.28	1.333	0.778	3.02	1.333	1.050	1.151	2.14
1.333	0.7813	2.23	0.667	.408	2.24	1.333	0.417	0.935	2.51
0.667	.418	2.18	.4444	.275	1.48	0.3333	1.040	.632	2.58
.4444	.280	1.30	.3333	.212	1.59	.3333	0.402	.375	2.01
.3333	.216	1.40	.2667	.174	2.01	.2222	.700	.432	2.82
.2667	.177	1.64	.2222	.149	2.17	.2222	.536	.365	2.58
.2222	.151	2.39	.1667	.109	0.097[a]				
.1667	.114	2.34							
.1333	.0935	2.17							
Average		1.99			2.08				2.44

[a] Omitted in taking the average.

Subtraction of $(Fe(OH)^{++})$ and $(Fe(OH)_2^+)$ from m gives the concentration of the ferric ion, (Fe^{+++}), while the sum of $(Fe(OH)^{++})$ + 2 $(Fe(OH)_2^+)$ gives the concentration of the hydrogen ion, (H^+). k_1 is then finally obtained from the equation $k_1 = (Fe(OH)^{++})(H^+)/(Fe^{+++})$. These data and the resulting values are given in Table V. They show no trend toward higher values at lower concentrations, so average values have been taken for each set of measurements. The grand average 2.2×10^{-3} is confirmatory of the values obtained from the measurements with the glass electrode. However, since a different assumption as to the conductance of the unhydrolyzed and partially hydrolyzed salts, particularly $Fe(OH)Cl_2$, would have given somewhat different values of k_1, no great weight can be attached to this confirmatory evidence.

On the basis then of our measurements with the glass electrode, giving particular weight to the results with added acid, the best value of k_1 at 25° appears to be 2.5×10^{-3} in a 3.3×10^{-4} M solution, corresponding to $k_1 = 3.5 \times 10^{-3}$ at zero ionic strength. We have adopted this value in our calculations rather than the considerably

---

[12] For $LaCl_3$ see Jones and Bickford, This Journal, **56**, 602 (1934), and page 974 of our prior communication.[1] For $SrCl_2$ and NaCl see "I. T. C.," Vol. VI, 1929, p. 233.

higher value of Bray and Hershey because of the directness and concordance of our experimental evidence; however, the conclusions which we draw from our calculations would not be significantly altered if the higher value were employed. The value of k_2 has been fixed as approximately 2×10^{-5}, chiefly by our measurements in dilute solutions as explained above. For k_3 a value of fifty times smaller than this, namely, 4×10^{-7}, has been assumed arbitrarily. The uncertainty of this assumption does not affect our conclusions at all except in one particular which will be explained later.

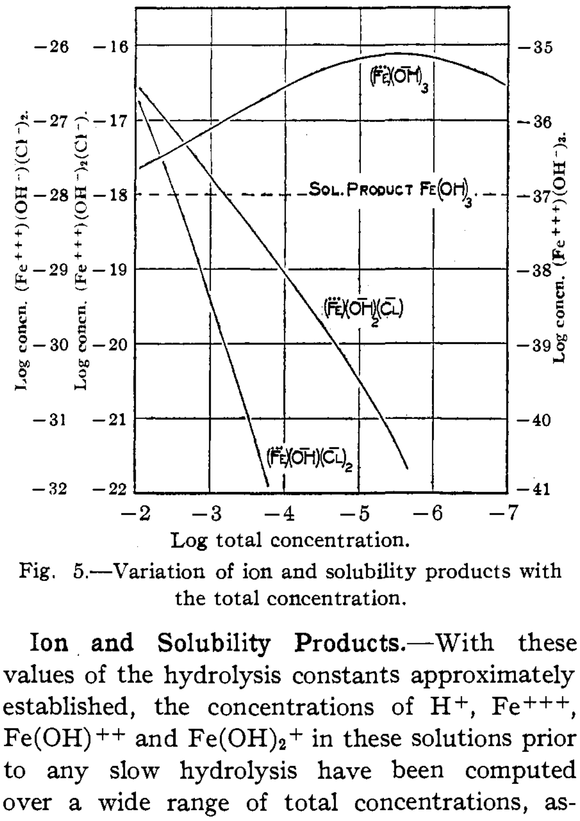

Fig. 5.—Variation of ion and solubility products with the total concentration.

Ion and Solubility Products.—With these values of the hydrolysis constants approximately established, the concentrations of H^+, Fe^{+++}, $Fe(OH)^{++}$ and $Fe(OH)_2^+$ in these solutions prior to any slow hydrolysis have been computed over a wide range of total concentrations, assuming complete ionization of the strong electrolytes present. This computation has been carried out conveniently by a process of successive approximation. The relatively insignificant concentration of un-ionized ferric hydroxide was neglected and preliminary values guessed for the concentrations of H^+ and $Fe(OH)_2^+$, the latter also being relatively small and constant. Tentative values for $Fe(OH)^{++}$ and Fe^{+++} could then be computed easily and from them in turn more accurate values for H^+ and $Fe(OH)_2^+$ obtained. A few repetitions of this procedure usually sufficed.

From these values the ion-products of the several hydrolysis products then could be obtained and curves depicting them are shown in Fig. 5. It can be seen that the ion-products for $Fe(OH)^{++}$ and $Fe(OH)_2^+$ both decrease rapidly with the dilution, while that for $Fe(OH)_3$ increases steadily over the range accessible to experiment, reaching a maximum at a salt concentration of about 3×10^{-6} *M* and decreasing in still more dilute solutions.

The solubility product of ferric hydroxide was derived from the observation, to be discussed more fully later, that the initial velocity of hydrolysis in solutions of ferric chloride containing increasing amounts of acid in all cases approaches zero when the concentration of undissociated ferric hydroxide is approximately 2×10^{-9} *M*. This concentration multiplied by the dissociation constant of ferric hydroxide (*i. e.*, $10^{-42}/k_1k_2k_3$) gives for the solubility product $(Fe^{+++})(OH^-)^3$ the value 1×10^{-37} shown by the horizontal broken line in Fig. 5. It should be pointed out, however, that the concentration 2×10^{-9} *M* represents the solubility of the initially highly dispersed colloidal ferric hydroxide rather than that of the aged colloid in the final solution.

Figure 5 furnishes the key to an understanding of this type of slow hydrolysis. It shows that of the hydrolysis products suggested by Goodwin as controlling the tempo of this reaction the only one whose ion-product increases with increasing dilution is ferric hydroxide, so it is evidently this substance whose concentration determines the speed of the slow hydrolysis. Moreover, it shows that its ion-product in solutions more dilute than 0.1 *M* is always greater than the solubility product of the initially formed colloidal ferric hydroxide. Stated in terms of solubility, these curves show that all solutions of ferric chloride less concentrated than 0.1 *M* are supersaturated with respect to ferric hydroxide and the supersaturation increases with increasing dilution of the ferric salt. In other words, the slow hydrolysis of ferric salt is evidently a slow precipitation of ferric hydroxide from supersaturated solution. It should only take place in solutions more dilute than 0.1 *M* and its speed should increase with increasing dilution. This is, of course, just what is observed.

Quantitative Correlation.—In order to subject this explanation to a more quantitative test, we have compared the speed of hydrolysis at successive intervals during the slow hydrolysis in every solution of ferric chloride in which measurements with the glass electrode were made, with the then prevailing concentration of *dissolved undissociated* ferric hydroxide. The concentrations of the several ion species and the ferric hydroxide in these solutions were computed as in the case of the final equilibrium solutions by successive approximation. The computation of the concentration of the undissociated ferric hydroxide was based on the above mentioned reasonable but unsupported assumption as to k_3, the hydrolysis constant of the reaction $Fe(OH)_2^+ + H_2O \rightleftarrows Fe(OH)_3 + H^+$. Since only relative concentrations are here involved and since the concentration of ferric hydroxide is always proportional to k_3, no significant error is introduced here by the uncertainty of this assumption. The speeds of hydrolysis were obtained by plotting against the time the amounts of colloidal ferric hydroxide produced, as found by difference in the above computation, and taking the tangents of these curves at the measured points. In Fig. 6 these speeds of hydrolysis are in turn plotted against the corresponding concentrations of dissolved ferric hydroxide.

It can be seen from this figure that the curves, except for the initial portions of those representing the more concentrated solutions, are nearly parallel, straight lines and except at very low concentrations of ferric hydroxide lie in a relatively narrow band. This is emphatic evidence of the correctness of the above hypothesis, namely, that the progress of the slow hydrolysis is proportional to the degree of supersaturation of the ferric hydroxide in the solutions.

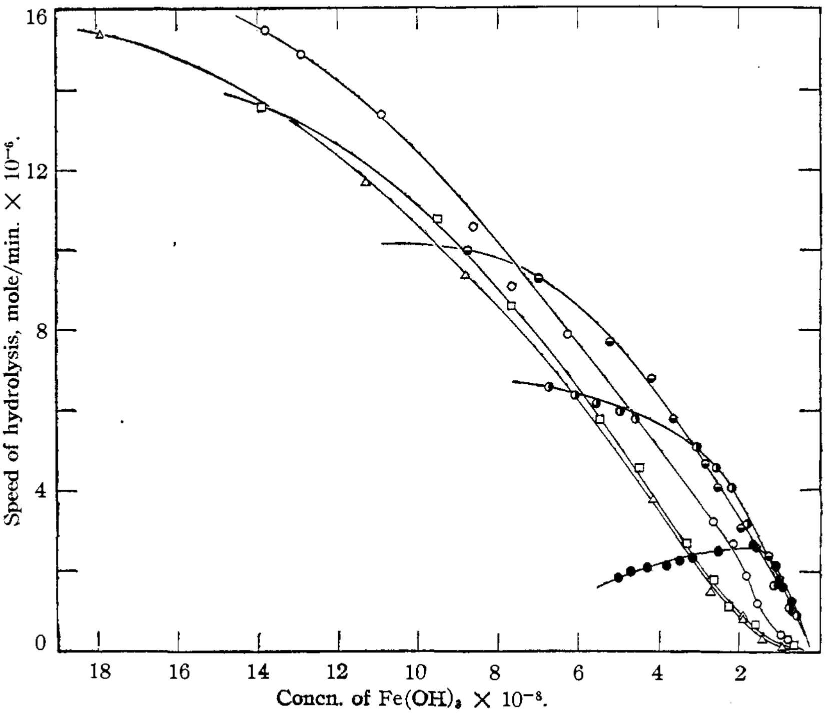

Fig. 6.—Variation of the speed of hydrolysis with the concentration of ferric hydroxide in ferric chloride solutions at 25°: ●, 0.01000 *N*; ◑, 0.00400 *N*; ◒, 0.00200 *N*; ○, 0.001000 *N*; □, 0.000667 *N*; △, 0.000500 *N*.

The lack of coincidence at low concentrations of ferric hydroxide, that is, when the slow hydrolysis is nearly completed, is also easily understood on the basis of this hypothesis. In Fig. 6 the curves for the more concentrated solutions in this region lie progressively somewhat farther to the right; which means that, at any given concentration of ferric hydroxide, the rate of hydrolysis in this region is greater the more concentrated the solutions. This is what is to be expected, since our earlier measurements[1] have shown that the more concentrated solutions of ferric chloride give rise to coarser colloidal particles of ferric hydroxide whose solubility is correspondingly less, ultimately becoming that of massive ferric hydroxide particles. Supersaturation is therefore greater in these solutions for the same concentration of ferric hydroxide and the velocity of hydrolysis at this point will be correspondingly greater.

The correctness of this interpretation may also be checked quite directly by an examination of the retarding effect produced by the subsequent addition of acid to solutions of ferric chloride undergoing slow hydrolysis as shown by the conductance data already presented in Fig. 9 of our earlier communication.[1] For this purpose we have plotted these data on a larger scale and from the slopes of the main and branch curves at the moment of addition of the acid, we obtain the speed immediately before and after the addition of acid, as given in the second and third columns of Table VI. We have then, from our electrometric measurements of the hydrogen ion activity during the slow hydrolysis, calculated by successive approximation as explained above, the concentration of undissociated ferric hydroxide in these solutions immediately before and after the addition of the acid. These values are given in the sixth and seventh columns of Table VI. The ratios of these two concentrations, given in the next to the last column, agree well with the observed ratios of the speeds in the respective solutions given in the final column of the table. This agreement is strongly confirmatory of the correctness of our interpretation.

TABLE VI

Time, min.	Speeds mols/mm. $\times 10^6$		(H^+) $M \times 10^4$		$(Fe(OH)_3)$ $M \times 10^9$		Ratios	
	Before	After	Before	After	Before	After	$Fe(OH)_3$ concns.	Speeds
2	9.5	3.3	3.78	5.70	12.9	5.6	2.3	2.8
3	7.5	3.1	3.97	5.86	10.9	4.97	2.2	2.4
4	6.6	2.9	4.24	6.06	9.6	4.46	2.1	2.3
15	2.9	1.3	5.88	7.75	3.36	1.80	1.9	2.2
60	0.54	0.30	7.45	9.28	1.22	0.73	1.7	1.8

The Initial Stages of the Slow Hydrolysis.—It was pointed out above that, while the slow hydrolysis proceeds in the dilute solutions at a rate proportional to the supersaturation of the ferric hydroxide and, when it is once under way, in the more concentrated solutions also, this is *not* the case during the initial stages of the hydrolysis of the more concentrated solutions, when the period of induction in the changes of conductance, color and hydrogen ion concentration referred to previously, is observed. It is evident that in these more concentrated solutions at the start an additional factor is involved which is not operative in dilute solutions or in the later stages of the hydrolysis in the concentrated solutions.

A reasonable explanation of this initial phenomenon is as follows. The slow hydrolysis during most of its course proceeds by the deposition of dissolved ferric hydroxide upon nuclei (amikrons and submikrons) of this substance already extant, so that the particle size of these colloidal solutions of ferric hydroxide progressively increases. This process of deposition, which is responsible for most of the conversion so far as amount of material is concerned, is, however, necessarily preceded by a process of nuclei formation, that is, one in which at a multitude of points in the solution two or more molecules of ferric hydroxide coalesce to form particles which can grow by accretion.

This initial process of nuclei formation is not observed in dilute solutions of ferric salts at 25° since, by the time the first measurement is made, it will be progressing at a rapid rate and indeed by that time may have progressed so far that it has become of subordinate importance as compared with the process of particle growth then already in full swing. In concentrated solutions at 25°, however, where the supersaturation of the ferric hydroxide is relatively slight, the initial process of nuclei formation is much slower and there is, therefore, at first little opportunity for growth by accretion, with a consequent negligible rate of change in the conductance, color and hydrogen ion concentration of the solution. However, the number of nuclei becomes steadily greater and accretion is correspondingly accelerated so that ultimately slow hydrolysis takes place at a considerable rate even in a solution which at the outset appeared stable.

This explanation of the induction period and of the initial abnormalities exhibited by these solutions as due to the process of nuclei formation is supported by the accelerating effect which Goodwin[8] obtained by the prior addition of ferric hydroxide hydrosol. It is also compatible with Wagner's[13] observation, confirmed by our previous measurements[1] of the marked inhibiting effect of gelatin upon the slow hydrolysis.

If this explanation of the induction period is correct, it should be possible to apply to our observations during the initial period of the slow hydrolysis the equation of v. Smoluchowski[14] covering the coagulation of colloidal particles, whose correctness has already been attested by measurements made on several other quite diverse colloidal systems.[15] According to it, the total number of particles present in one cubic centimeter undergoing coagulation in the time t, in seconds, is

$$\Sigma v = v_1 + v_2 + v_3 \ldots = \frac{v_0}{1 + 4\pi A D \xi v_0 t}$$

where v_0 is the original number of single (primary) particles, v_1, v_2, v_3, etc., are the numbers of single, double, triple, etc., particles present. ξ is the fraction of the collisions which results in permanent

---

(13) C. H. Wagner, *Monatsh.*, **34**, 102 (1913).

(14) Von Smoluchowski, *Physik. Z.*, **17**, 587–599 (1916), and *Z. physik. Chem.*, **92**, 125 (1917).

(15) (a) Zsigmondy, *ibid.*, **92**, 600 (1917); (b) Westgren and Reitstötter, *ibid.*, **92**, 750 (1918); *J. Phys. Chem.*, **26**, 537 (1922); (c) Kruyt and van Arkel, *Rec. trav. chim.*, **39**, 656 (1920); (d) Lacks and Goldberg, *Kolloid-Z.*, **31**, 116 (1922); (e) Ehrenhaus and Wintgen, *Z. physik. Chem.*, **104**, 301 (1923); (f) Teorila, *Kolloidchem. Beihefte* **22**, 191 (1926); **24**, 1 (1927); **27**, 44 (1928).

union, A the radius of the sphere of attraction of the particles and D the diffusion coefficient in the Einstein–Stokes equation, $D = RT/6\pi N\eta r$, in which, in turn, R is the gas constant, T the absolute temperature, N the number of molecules per gram molecule, η the coefficient of viscosity of the solution at T°K. and r the radius of the primary particles. Substituting known numerical values (in cm.-sec.) the above equation becomes as applied to our systems

$$\Sigma v = \frac{v_0}{1 + 3.06 \times 10^{-12}\,(A/r)\xi v_0 t}$$

When this equation is differentiated with respect to t

$$\frac{\mathrm{d}\Sigma v}{\mathrm{d}t} = \frac{3.06 \times 10^{-12}(A/r)\xi v_0^2}{(1 + 3.06 \times 10^{-12}(A/r)v_0\xi t)^2}$$

At the outset, therefore, when $t = 0$

$$\frac{\mathrm{d}\Sigma v}{\mathrm{d}t} = -3.06 \times 10^{-12}\,\frac{A}{r}\,\xi v_0^2$$

Converting this into concentration, expressed as gram molecules per liter (c) per minute we obtain

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -1.11 \times 10^{11}\,\frac{A}{r}\,\xi c^2$$

That is, the initial speed of the slow hydrolysis should be proportional to the *square* of the concentration of the substance undergoing coagulation, *i. e.*, the ferric hydroxide. Moreover, since no coagulation would occur in a saturated solution (or would be balanced by an equally rapid dissolution of the solute), the effective concentration is the excess concentration, *i. e.*, the extent of supersaturation of the ferric hydroxide.

To test this conclusion we have ascertained the initial rates of hydrolysis from the slopes of our curves for the molar conductance of ferric chloride solutions at 25° extrapolated to zero time. To express these velocities in moles per liter per minute, we have divided them by the average difference between the molar conductivity of ferric chloride and the resultant three moles of hydrochloric acid at these concentrations and have then multiplied by the molar concentration. These values are listed in Table VII. We have computed the initial concentration of ferric hydroxide in these solutions by the process of successive approximation using the same values of the three hydrolysis constants as previously set forth. When these velocities in moles per liter per minute are plotted against the computed initial concentrations of the ferric hydroxide, the points, for the most part, lie closely upon a smooth curve. This curve becomes asymptotic to the axis of concentrations at about 2 × 10^{-9} M and we have taken this limiting value as the solubility of the ferric hydroxide in these initial solutions. Subtracting it from the computed concentrations, we obtain what were called above the effective concentrations of the ferric hydroxide as listed in the sixth column of Table VII. Finally, when the velocities are divided by the squares of the effective concentration, the values of the resulting velocity constant given in the last column are obtained. Except in the most concentrated and most dilute solutions where an exact determination of the initial velocities is out of the question these values are quite constant, the average deviation of the individual values from the mean being only about 10% over a range of velocities varying by more than 100-fold. This agreement with the requirements of the von Smoluchowski theory confirms the view that the initial step in the slow hydrolysis of ferric chloride is a slow coagulation of the ferric hydroxide particles.

Table VII

Velocity of Initial Slow Hydrolysis of Ferric Chloride

Concn. $FeCl_3$ $M \times 10^3$	Concn. HCl added $M \times 10^3$	Initial velocity mhos/min.	Initial velocity mols/min. $\times 10^6$	Concn. $Fe(OH)_3$ $M \times 10^9$	Concn. $Fe(OH)_3$ −2 $M \times 10^9$	Velocity constant K $\times 10^{-10}$
0.1333	0.0	30.0	14.0	44.0	42.0	(0.86)
.1667	.0	21.0	12.3	37.6	35.6	(.98)
.2222	.0	18.0	13.3	30.7	28.7	1.76
.2667	.0	11.6	10.8	26.9	24.9	1.74
.3333	.0	9.0	10.5	22.7	20.7	2.44
.4444	.0	4.5	7.0	18.5	16.5	2.53
.6667	.0	1.3	3.0	13.8	11.8	2.16
1.333	.0	0.19	0.89	8.7	6.7	1.98
3.333	.0	.014	.16	5.2	3.2	1.57
0.2222	.0163	16.0	12.5	27.1	25.1	1.98
.2222	.0434	11.0	8.6	22.3	20.3	2.08
.2222	.1060	4.6	3.6	15.0	13.0	2.12
.2222	.1970	1.5	1.17	9.2	7.2	2.28
.2222	.337	0.11	0.086	5.1	3.1	(0.90)
.2222	.400	.058	.045	4.0	2.0	(1.12)
.2222	.536	.028	.022	2.6	0.6	(6.1)
.3333	.0171	6.8	8.0	20.9	18.9	2.24
.3333	.0512	3.8	4.4	17.4	15.4	1.85
.3333	.102	1.85	2.16	13.6	11.6	1.61
.3333	.223	0.58	0.68	8.2	6.2	1.77
.3333	.402	.080	.094	4.5	2.5	1.50
.3333	1.04	.020	.023	1.0	..	..
1.333	0.046	.15	.70	7.9	5.9	2.01
1.333	.115	.042	.20	7.0	5.0	(0.80)
1.333	.222	.016	.075	5.9	3.9	(.50)
						Average 2.0 ±0.23

It is also of interest to compare the absolute magnitude of the constant $[1.11\ (A/r\ \xi) \times 10^{11}]$ in the theoretical equation with that of the constant found experimentally (2.0 × 10^{10}). In the several cases where this theory has been experimentally tested and verified, A/r has been found to have a value between 2 and 3, indicating that the particles are nearly in contact when within the sphere of each other's attraction. Taking 2.5 then for this ratio, a value of 0.07 must be assigned to ξ for the two constants to become identical. That is, it must be assumed that only 7% of the collisions of the ferric hydroxide molecules result in a permanent union. This is within the range of values found for ξ in other slow coagulations.[15b,c,f]

No great weight should, however, be attached to the exact ratio of the two constants because the experimental constant is based upon calculated values of the concentration of the ferric hydroxide which are in turn based on an uncertain assumption as to the final (third) hydrolysis constant of ferric hydroxide. A slight change in this constant and hence in the computed concentrations of the ferric hydroxide would produce a considerable change in the absolute value of the velocity constant. It would not, however, affect the constancy of this constant.

The Solubility of Ferric Hydroxide.—The final solution in which a stationary state has been reached may be looked upon as saturated solutions of ferric hydroxide in solutions of hydrochloric acid and of ferric chloride of known hydrogen ion and approximately known ferric ion concentration. These latter concentrations have been computed from the above established values of k_1 and k_2 by a process of successive approximation with the further assumption justified by evidence previously given[1] that the colloidal ferric hydroxide in these solutions adsorbs only a negligible amount of chloride. From these values the solubility products of ferric hydroxide in the final solution have been computed. They are listed in the second column of Table VIII.

The only approximately trustworthy values in the literature for the solubility product of ferric hydroxide are those based on electrometric measurements made during the titration of ferric salts with alkali. They are in general somewhat larger than our values and are quite discordant. Thus Jellinek[16] found 1×10^{-38}, Elder[17] 3 to 400×10^{-38} and Kriukov[18] 10 to 3000×10^{-38} with a preferred value of 30×10^{-38}. Any strict comparison of our values with these earlier values is of doubtful utility as the conditions attending them were different and not always sharply defined; moreover, it is not certain that they represented real equilibria.

Our own values for the solubility show a decided trend toward smaller values in more concentrated solutions. It appears not unlikely that this trend may be explained on the basis of a reasonable variation in the size of the particles of colloidal ferric hydroxide.

To test this, we have first derived the solubilities of undissociated ferric hydroxide in these solutions from the above values of the solubility product and from our assumed value for the third hydrolysis constant of ferric hydroxide. They are listed in the third column of Table VIII.[19]

From them we have calculated, by means of the Ostwald equation as modified by Freundlich,[20] $\ln L/L_1 = 2M\sigma/rRTd$ what the diameters of the particles would have to be to account for the observed variation in the solubilities. In this equation L_1 is the solubility of large particles, L the solubility of particles of radius r, M the molecular weight, d the density and σ the surface tension of the solid against its saturated solution. Taking d as 4.4, σ as 1150 dynes/cm. (the average of all such surface tensions so far measured)[21] and L_1 as 0.17×10^{-10} M, this equation becomes

$$r = \frac{8.9 \times 10^{-7}}{\log L + 10.7796}$$

The values of the diameters of the particles ($2r$) computed by means of this equation are given in the last column of Table VIII.

TABLE VIII

VARIATION OF SOLUBILITY WITH PARTICLE SIZE

Total concn. $\times 10^3 M$	Soly. product $(\text{Fe}^{+++})(\text{OH})_3$ $\times 10^{38} M$	Soly. Fe(OH)_3 $\times 10^{10} M$	Total soly. $\text{Fe(OH)}_3 + \text{Fe}^{+++}$ $\times 10^{10} M$	Diameter particle $2r$ mμ
...	[0.13]	[0.17]	[1.00]	...
3.333	.137	.18	1.0	510
1.333	.20	.31	1.2	66
0.667	.37	.67	1.8	29
.333	.93	1.7	3.1	18
.222	1.5	2.7	4.2	15
.167	1.7	3.2	4.8	14

It should be pointed out that, while the absolute values of the solubility are uncertain be-

---

(16) K. Jellinek and H. Gordon, *Z. physik. Chem.*, **112**, 237 (1924).

(17) Elder, *Trans. Am. Electrochem. Soc.*, **57**, 383 (1930).

(18) P. A. Kriukov and G. P. Awsejewitsch, *Z. Elektrochem.*, **39**, 884 (1933).

(19) As a matter of interest we have also computed the corresponding *total* solubilities of ferric hydroxide and these are listed in the fourth column. It can be seen that ferric hydroxide is between $^1/_3$ and $^2/_3$ dissociated in these solutions.

(20) Freundlich, "Kapillarchemie," Vol. 1, 4th ed., Leipzig, 1930, p. 218.

(21) Glasstone, *J. Chem. Soc.*, **119**, 1689 (1922); Dundon, THIS JOURNAL, **45**, 2658 (1923).

cause of their direct dependence upon the assumed value of the third hydrolysis constant of the ferric ion, the values for the diameters of the particles are free from this uncertainty since they depend on the relative and not on the absolute solubility. They are, however, directly dependent on the assumed value for the surface tension of the solid.

The diameters of particles of ferric hydroxide sols prepared by boiling dilute solutions of ferric chloride have been measured by Nichols, Kraemer and Bailey.[22] They found that the particles in each solution were fairly uniform in size, the mean diameters in 0.003, 0.005 and 0.037 *M* solutions being 4, 5.2 and 8.8 mμ, respectively, after one hour's boiling. These diameters are considerably smaller than our values as listed in Table VIII, which is what would be expected from our observations on the clarity and stability of solutions hydrolyzed at higher temperatures. Their variation with concentration is in the same direction as that of our own values.

The only information as to the size of the colloidal particles formed by hydrolysis of ferric salt solutions at *room temperature*, so far as we are aware, is based on the observations of Bachmann[23] who, using a slit ultramicroscope, was unable to see any particles in a 0.000167 *M* solution of ferric chloride, although he observed a pale, bluish Tyndall cone whose light was linearly polarized. Using an immersion ultramicroscope, submikrons were visible. These particles were therefore very near the limit of visibility and as lyophobic, oxide sols should have had diameters of about 10 to 20 mμ.[24] This estimate includes the diameter given in Table VIII for this solution. It appears reasonable therefore that the observed variation in the solubility product in the different solutions of hydrolyzed ferric chloride is due to a variation in particle size.

Summary

1. The hydrogen ion concentration of the dilute ferric salt solutions during their slow hydrolysis has been measured by means of the glass electrode. The curves thus obtained are consonant with those obtained previously in corresponding measurements of conductance and color.

2. From the extrapolated initial values of the hydrogen ion concentration reasonably concordant values for the first and second hydrolysis constants of the ferric ion have been computed and from these, with permissible assumptions, the individual concentrations of unhydrolyzed, partially and completely hydrolyzed ferric ions over a wide range of total concentration have been calculated. These calculations show that undissociated ferric hydroxide is the only substance in these solutions whose actual concentration increases with decreasing over-all concentration of the ferric salt.

3. On this basis an extension of Goodwin's explanation of this phenomenon has been advanced according to which, as soon as the ferric salt dissolves, a rapid reversible hydrolysis ensues giving rise to a variety of hydrolysis products but in particular to a dilute, nevertheless supersaturated, solution of *ferric hydroxide*. The coagulation of this substance to form colloidal ferric hydroxide is the controlling, relatively slow step, in this reaction.

4. Similar calculations of the concentration of the undissociated ferric hydroxide at successive intervals during the slow hydrolysis have been made and it has been found that the rate of slow hydrolysis in all the solutions studied is in general proportional to this excess concentration of the undissociated ferric hydroxide over its solubility, *i. e.*, to its degree of supersaturation. This same proportionality persists even when extra acid is added after the start of the slow hydrolysis.

5. Departure from this direct proportionality occurs in every case during the initial stages of the slow hydrolysis. Here the speed of hydrolysis evidently is limited by the rate of formation of nuclei and in these cases it has been found that the speed, over a wide range of concentrations, is proportional to the *square* of the concentration of the ferric hydroxide in accordance with the requirements of the von Smoluchowski theory of rapid coagulation.

6. Departure from direct proportionality is observed also at the very end of the slow hydrolysis in the acidified and in the more concentrated solutions. Here the solubility of the ferric hydroxide is reduced considerably as a result of increased particle size, so that in spite of the low concentration of the ferric hydroxide the slow hydrolysis continues.

Cambridge, Mass. Received January 12, 1938

---

[22] Nichols, Kraemer and Bailey, *J. Phys. Chem.*, **36**, 331 505, (1932).

[23] W. Bachmann, *Z. anorg. Chem.*, **100**, 83 (1917).

[24] R. Zsigmondy, "Kolloidchemie," 5th ed., Vol. 1, Leipzig, 1925, pp. 12–17.